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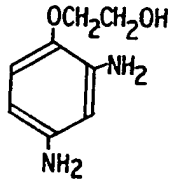
(54) OXIDATION DYE COMPOSITIONS

(71) We, BRISTOL-MYERS COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, having offices located at 345 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to a composition and a method for dyeing keratin fibers, and more particularly for dyeing human hair, either in the form of a wig or as natural hair on the human head, using a substituted m-phenylene diamine.

According to the present invention, we provide an oxidation dye composition comprising an oxidation hair dye concentrate containing a tinctorially effective amount of a para component and a meta component; said para component and meta component being reactive with each other in the presence of an oxidizing agent to form a coloured dye on hair; said meta component being a substituted m-phenylene diamine of the formula:



or a salt thereof. The term "oxidation hair dye concentrate" is explained below, and the term "para component" is employed herein with its ordinary meaning as understood by those skilled in the hair dyeing art. If a salt of a meta component of the foregoing formula is employed, this salt may for example be a salt with HCl or H_2SO_4. The salt is desirably non-toxic.

The invention also includes a method of dyeing human hair, which comprises mixing the oxidation dye composition of the invention with an oxidizing agent, applying an effective dyeing amount of the resulting mixture to human hair, and allowing said mixture to remain in contact with said hair for a period of time to effectively dye said hair.

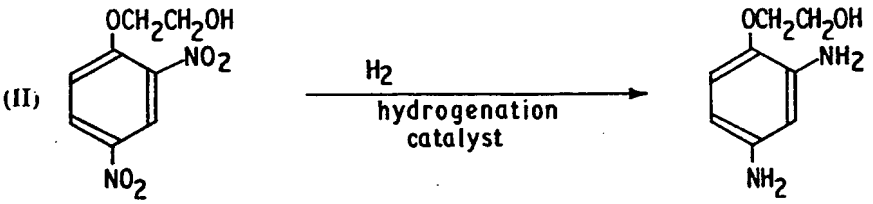
It is known that, in the present state of the hair dye art, only the so-called oxidation dyes give permanent dyeing in all shades. Practically all permanent dyes are formulated as oxidation dye compositions which give a large variety of shades especially the natural ones. These dye compositions are formulated as mixtures of para components as, for example, aromatic diamines, or aminophenols; and meta components as, for example, m-toluenediamine, m-phenylenediamine. The mixture of para and meta components reacts on the hair in the presence of hydrogen peroxide to form colors.

It has now been found that a compound of the above formula or its salts may be effectively used as meta components in oxidation dye compositions. The shades obtained have acceptable resistance to repeated shampooings with a minimum change in color and give adequate coverage. Without attaching any value judgment

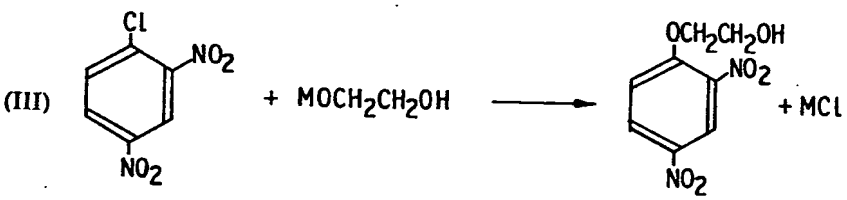
to this finding, it is of interest to note that the compound encompassed in the above formula assayed as being essentially non-mutagenic to certain mutation-prone strains of Salmonella typhimurium.

The present invention thus provides dye compositions for dyeing keratin fibers and particularly hair dye compositions of the permanent type containing the above identified meta component.

The substituted m-phenylenediamines employed in accordance with the present invention can be readily prepared by the reductive hydrogenation of the corresponding dinitro compounds. This can be illustrated by the following equation:

(II) 

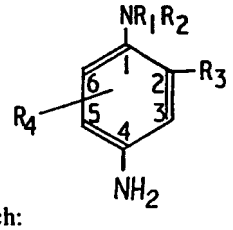
The starting materials for reaction (II) can be made by reacting 2,4-dinitrochlorobenzene with the appropriate alkali metal alcoholate e.g. the potassium alcoholate. This reaction can be depicted by the following equation wherein M is an alkali metal e.g. potassium.

(III) 

In the hair dye trade, it is customary to supply oxidation dyes in two parts; the first comprising a mixture of dyes and dyeing aids, etc., herein referred as the oxidation (hair) dye concentrate, and the second being the developer. The concentrate is adapted to be mixed with the developer just before the product is used. The compound of the first formula herein, and its salts, are intended for use mainly as meta components in an oxidation (hair) dye concentrate. When used for this purpose, these compounds may be present in dye concentrates in varying amounts depending upon the shade desired, the nature and concentration of other components, etc. In general, however, it will comprise from 0.001 to 3.0% by weight, and preferably from 0.01 to 2.0% by weight, based on the weight of the concentrate.

The aforesaid dye concentrate compositions will usually be aqueous alkaline compositions that contain, in addition to the meta component of the first formula herein, at least one para component. Optionally, such concentrates may also contain such things as modifier dye intermediates, nitro dyes, soaps, surfactants, thickening agents, antioxidants and organic solvents. Furthermore, these aqueous concentrates may take various forms such as solutions, flowable liquids, pastes, creams or gels.

Illustrative of the para components that may be used in this invention are the following: p-toluenediamine, p-aminophenol, p-aminodiphenylamine, 4 - 4' - diaminodiphenylamine, p-phenylenediamine, 2,6 - dimethyl - p - phenylenediamine, 2,5-diaminopyridine. Of special interest is a class of para components described by the formula:



or its non-toxic salts, in which:

R_1 is alkyl or hydroxyalkyl;
R_2 is hydrogen or hydroxyalkyl;
R_3 is hydrogen, alkyl, alkoxy or halogen;
R_4 occupies any one of the remaining positions on the benzene radical and is hydrogen, alkyl, alkoxy or halogen;
providing that R_2 is hydrogen when R_3 is alkyl, alkoxy or halogen and providing that at least one of R_2, R_3 or R_4 is other than hydrogen. Preferably the alkyl groups or alkyl moieties contain 1 to 6 carbon atoms, and preferably the hydroxyalkyl contains from 1 to 3 hydroxy groups. The halogen may be Cl, Br, F or I.

In addition to the meta components mentioned above, the oxidation dye concentrates of this invention may contain other modifier dye intermediates. These include such compounds as the m-aminophenols, compounds containing active methylene groups, phenols, etc. m-Aminophenols can give either indophenols or indamines on oxidative coupling with para components. The products are usually violet in color and are used in modifying shades. Examples of aminophenols useful herein are 2,4-diaminophenol, m-aminophenol, aminoresorcinol, 1,5-aminohydroxynaphthalene and 1,8-aminohydroxynaphthalene.

Compounds containing active methylene groups are also capable of reacting with the oxidatively activated para components. The products are imino compounds of various types and are yellow or red in color. Examples of active methylene compounds employable in the present invention are 3 - methylpyrazolone - (5), 1 - phenyl - 3 - methylpyrazolone - (5), 1,3 - dimethylpyrazolone - (5), acetoacetic acid anilide, benzoylacetotoluide and nicotinoylacetanilide.

Still other oxidation dye intermediates, i.e. modifiers, may be present in the concentrates of this invention which produce colored products under oxidative conditions by more complex mechanisms. These mechanisms may include one or more of self-coupling, or coupling with the para components or with other intermediates present. Among these may be mentioned hydroquinone, catechol, 1,5-naphthalenediol, o-phenylenediamine, o-aminophenol.

Phenols react with para components in the presence of oxidizing agents to produce indophenols. These are usually blue or violet compounds, although resorcinols give yellow or brown colored compounds under these conditions. The brown colors obtained from the reaction of resorcinols are commonly used to produce the depth of a shade. Examples of phenols useful in oxidation dye concentrates of this invention are pyrogallol, resorcinol, pyrocatechol and alpha-naphthol.

It is sometimes desirable to add, to said oxidation dye concentrate, dyes which are already colored i.e. which do not require an oxidizing agent for color development. These are generally added for blending purposes to obtain natural looking colors in the final dyeing operation. One class of dyes which may be used for this purpose is the nitro dyes and this component is generally referred to herein as the nitro dye component. A large number of nitro dyes are known in the prior art which are suitable for this purpose. The only limitation that is placed on a nitro dye to be useful in the present invention is that it be one whose color is not destroyed by the oxidizing agent used in the final color development of the oxidizable components. By way of illustrating suitable nitro dyes, mention may be made of the following: 4 - nitro - o - phenylenediamine, 2 - nitro - p - phenylenediamine, 4 - nitro - 2 - aminophenol, 5 - nitro - 2 - aminophenol, 2 - nitro - 4 - aminophenol and picramic acid.

The pH of the oxidation dye concentrate employed in accordance with this invention will generally be on the basic side e.g. 8—11. It is preferred, however, that this pH be in the range of 9—10.

Any of a wide variety of alkalizing agent can be used to adjust the pH of the oxidation dye concentrate on the basic side. Ammonium hydroxide, because of its freedom from toxicity over a wide concentration range and its economy, is an acceptable alkalizing agent. However, there can be used in place of, or together with, ammonia any other compatible ammonia derivative as an alkalizing agent, such as an alkylamine, such as ethylamine, or triethylamine, or alkanolamine, such as monoethanolamine or diethanolamine.

Soaps may also be present in the concentrates of this invention. By way of illustration, there may be mentioned the sodium, ammonium or potassium salts of lauric, stearic, palmitic, oleic, linoleic or ricinoleic acid. The soaps may be present to the extent of 5 to 35% of the weight of the oxidation dye mixture, and preferably 15 to 25%.

Surface active agents are also useful in the present composition of this invention. These will usually be water-soluble surface active agents that can be anionic, non-ionic, or cationic. Illustrative of the various types of water-soluble surface active agents, there can be mentioned: higher alkylbenzenesulfonates; alkylnaphthalenesulfonates; sulfonated esters of alcohols and polybasic acids; taurates; fatty alcohol sulfates; sulfates of branched chain or secondary alcohols; and alkyl dimethylbenzyl ammonium chlorides. Illustrative of specific surfactants there can be mentioned: sodium lauryl sulfate; polyoxyethylene lauryl ester; myristyl sulfate; glyceryl monostearate; sodium salt of palmitic methyl taurine; cetyl pyridinium chloride; lauric diethanolamide; polyoxyethylene stearate; stearyl dimethyl benzyl ammonium chloride; dodecyl benzene sodium sulfonate; nonyl naphthalene sodium sulfonate; dioctyl sodium sulfosuccinate; sodium N-methyl-N-oleoyl taurate; oleic acid ester of sodium isothionate; sodium dodecyl sulfate; and the sodium salt of 3,9 - diethyl - tridecanol - 6 - sulfate. The quantity of water-soluble surface active agent when present can vary over a wide range, such as that of from 0.5% to 30% by weight of the composition, and preferably 1—10%.

Various organic solvents may also be present in the oxidation dye concentrate for the purpose of solubilizing a dye intermediate or any other component which may be insufficiently soluble in water. Generally, the solvent selected is such as to be miscible with water and innocuous to the skin, and includes for example, ethanol, isopropanol, glycerine, ethylene glycol, propylene glycol, ethylene glycol, monoethyl ether, diethylene glycol, and diethylene glycol monoethyl ether. The amount of solvent used may vary from 1 to 40% of the oxidation dye mixture, and preferably 5 to 30%.

A thickening agent can also be incorporated in the present dye concentrate. In this connection, mention may be made of sodium alginate or gum arabic, or cellulose derivatives, such as methylcellulose, hydroxyethylcellulose, or the sodium salt of carboxymethylcellulose, or acrylic polymers, such as polyacrylic acid sodium salt, or inorganic thickeners, such as bentonite. The quantity of thickening agent when present can vary over a wide range such as that of from 0.5% to 5% and preferably from 0.5% to 3% by weight.

It is also useful to use an antioxidant in the present oxidation dye concentrate. By way of illustrating this, mention may be made of sodium sulfite, thioglycollic acid, sodium hydrosulfite, and ascorbic acid. The quantity of antioxidant that may be contained in the present oxidation dye composition will usually be in the range of from 0.05% to 1% by weight based on the total weight of the oxidation dye composition.

Water is ordinarily the major constituent of the present concentrate and can vary over a wide range dependent in large measure on the quantity of other additives. Thus, the water content can be as little as 20%, and is preferably from 30 to 90%.

The dye concentrates of this invention are preferably aqueous compositions. The term "aqueous composition" is used herein in its usual generic sense as embracing any water-containing composition embodied in this invention. This includes true solutions or mixures of the dye in an aqueous medium, either alone or in conjunction with other materials, which are also dissolved or dispersed in the aqueous medium. The dye may be colloidally dispersed in the medium or may merely be intimately mixed therein.

To further illustrate the various other modifiers, antioxidants, alkalizers and other adjuvants that may be incorporated in the oxidation dye mixture of this invention, reference is made to Sagarin "Cosmetics, Science and Technology" (1957), pages 505 to 507, Interscience Publishers, Inc., New York. The aqueous compositions of this invention may take many forms. Thus, they may be thin or thick flowable liquids, pastes, creams, or gels, for example.

To summarize the various components that may comprise the oxidation dye concentrate of this invention, Table I below is given. The percentages are given as percent by weight based on the total weight of the oxidation dye concentrate.

TABLE I

Components	% by Weight Preferred	Particularly Preferred
Para component	.001 to 5	.01 to 3.5
New meta component	.001 to 3.0	.01 to 2.0
Other oxidation dye intermediate	0 to 4	0.1 to 2
Nitro dyes	0 to 3	0.1 to 2
Soap	0 to 35	15 to 25
Surfactant	0 to 30	1 to 10
Thickening agent	0 to 5.0	0.05 to 3
Antioxidants	0 to 1.0	0.05 to 1
Organic solvents	0 to 40	5 to 30
Water QS to 100%		
Alkalizing agent to pH	8 to 11	9 to 10

The aforesaid oxidation dye concentrates of this invention are intended for use in conjunction with conventional oxidation dye "developers", which contain the oxidizing agent necessary to effect reaction to colored products. Typical developers that are useful for this purpose are aqueous solutions of hydrogen peroxide e.g. 5 to 12%, or high viscosity creams containing in addition, for example, nonylphenol polyethylene glycol or lauryl alcohol polyethylene glycol, in an amount of from 2 to 10% of the weight of developer, or crystalline peroxide such as urea peroxide or melamine peroxide.

In use, a quantity of the developer described above is mixed with a quantity of oxidation dye composition described previously. Usually, the amount of developer taken is far in excess of that required to oxidize the intermediates, the amounts taken being dependent on the form and concentration of the developer selected. The mixture is well shaken and applied to hair. It can be applied as a shampoo to the entire head, applied to one area of the hair, such as the roots and combed through the rest of the hair later. The mixture is allowed to remain on the head for a period of time and is then removed by shampooing. The normal time of application is 20 to 30 minutes, but application times of from 10 minutes to one hour can be used.

In one form of application of the compositions of this invention, the oxidation dye mixture is dispensed from an aerosol container under pressure of a suitable propellant. The foam so obtained is mixed with the developer, generally a solution of hydrogen peroxide, and applied to the hair as above.

The following Examples are given to further illustrate the present invention. It is to be understood, however, that this invention is not limited thereto. The words "Triton" and "Carbitol" appearing in the Examples are registered Trade Marks.

The following terms used in the Examples have the meaning indicated below:

Foamole A:
N,N-bis(2-hydroxyethyl)-linoleamide

Triton X-15:
Polyoxyethylene(1)octylphenyl ether

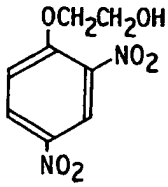
Igepal CO-430:
Polyoxyethylene(4)nonylphenyl ether

Dextrol:
Sulfated vegetable oil

Solulan C-24:
Polyoxyethylene(24)cholestrol ether

EXAMPLE 1

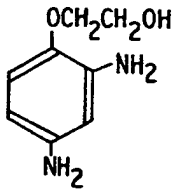
Preparation of 1-hydroxyethoxy-2,4-dinitrobenzene



To a 1000 ml. reaction flask equipped with a heater, stirrer, water trap and reflux condenser was added 400 ml. ethylene glycol and 11.2 gm KOH. The contents of the flask were heated to dissolve the KOH after which 100 ml. of benzene was added. The water in the reaction flask was distilled off and then the heating was discontinued. 40.5 gms. of 2,4-dinitrochlorobenzene was added to the reaction flask with stirring over a period of 1/2 hour. The reaction mixture was allowed to stand overnight after which it was vacuum filtered and dried. 31.30 gms of product was recovered which was dried in a desiccator over sulfuric acid. The dried material had a melting point of from 100 to 102°C and the following carbon, nitrogen and hydrogen analysis:

C: 42.30% N: 11.70% H: 3.37%
theory for $C_8H_8N_2O_6$=C: 42.10% N: 12.23% H: 3.51%

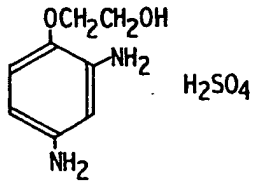
EXAMPLE 2
Preparation of 2,4-diamino phenyl ether of ethylene glycol



11.4 gms of 1 - hydroxyethoxy - 2,4 - dinitrobenzene, 1 gm of the hydrogenation catalyst comprising 5% platinum on carbon and 200 ml of ethanol was placed in a Parr hydrogenation bottle. Hydrogen was bubbled through the mixture until 20 lbs. of hydrogen was absorbed. The reaction mixture was then filtered while hot and the filtrate recovered. An excess of hydrogen chloride gas was bubbled through the filtrate to saturation and the product precipitated. This was then vacuum filtered and dried and 9.5 gms of product was obtained. The product was obtained as the hydrochloride salt of 2,4-diaminophenyl ether of ethylene glycol. This was analyzed for Cl, N, C and H content and the following values were obtained:

Cl: 28.47%; N: 11.57%; H: 5.97%;
C: 39.83%;
theory for $C_8H_{12}N_2O_2$, 2HCL: C: 38.83%; H: 5.80%; N: 11.61%;
Cl: 29.46%

Dyeouts were performed using compound II below as meta component:



The dye was used in the formulations given below:

Substance	% by Weight Ex. 3	Ex. 4	Ex. 5
Oleic acid	5	5	15.0
Isopropanol	20	20	9.2
Ammonium hydroxide	6	6	9.0
Sodium sulfite	0.2	0.2	0.2
Carbitol (25% ethylene glycol)	—	—	5.0
Foamole A	—	—	2.0
Propylene glycol	—	—	5.0
Triton X-15	—	—	6.0
Igepal CO-430	—	—	3.0

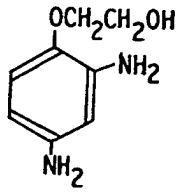
Substance	% by Weight Ex. 3	Ex. 4	Ex. 5
Dextrol	—	—	4.0
Solulan C-24	—	—	1.0
Fragrance	—	—	0.4
Erythrobic acid	—	—	0.2
EDTA	—	—	0.1
p-phenylenediamine	0.2	—	0.2
N,N-Bis-hydroxyethyl-p-phenylenediamine	—	0.2	—
Compound II	0.493	0.493	0.8
Water to	100	100	100

Each formulation above was mixed with an equal amount of 6% hydrogen peroxide and used to treat swatches of gray and bleached hair for 20 minutes. Results are summarized below:

Dye Formulation	Color on Gray Hair	Color on Bleached Hair
Ex. 3	Blue Violet	Deep Blue Violet
Ex. 4	Light Blue Green	Deep Blue
Ex. 5	Blue Violet	Deep Blue Violet

WHAT WE CLAIM IS:—

1. An oxidation dye composition comprising an oxidation hair dye concentrate containing a tinctorially effective amount of a para component and a meta component; said para component and meta component being reactive with each other in the presence of an oxidizing agent to form a colored dye on hair; said meta component being a substituted m-phenylenediamine of the formula:



or a salt thereof.

2. A composition according to Claim 1 wherein the hair dye concentrate is an aqueous composition.

3. A composition according to Claim 2 having a pH in the range of from 8 to 11.

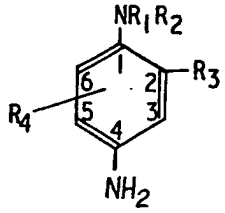
4. A composition according to Claim 3 in which the meta component comprises .001 to 3% by weight based on the total weight of the composition.

5. A composition according to Claim 4 in which the para component comprises .001 to 5% by weight based on the total weight of the composition.

6. A composition according to Claim 5 wherein the para component is selected from p-phenylenediamine, p-toluenediamine, N,N - bis(β - hydroxyethyl) - p - phenylenediamine and p-aminophenol.

7. A composition according to Claim 6 wherein said para component is N,N - bis(β - hydroxyethyl) - p - phenylenediamine.

8. A composition according to Claim 5 wherein said para component is of formula:



or its salts in which:

R_1 is alkyl or hydroxyalkyl;
R_2 is hydrogen or hydroxyalkyl;
R_3 is hydrogen, alkyl, alkoxy or halogen; and
R_4 occupies any one of the remaining positions on the benzene radical and is hydrogen, alkyl, alkoxy or halogen;
providing that R_2 is hydrogen when R_3 is alkyl, alkoxy or halogen and providing that at least one of R_2, R_3 or R_4 is other than hydrogen.

9. A composition according to Claim 1 including additionally an oxidizing agent capable of causing said para component to react with said meta component to form a colored dye.

10. A composition according to Claim 9 in which the para component is N,N - bis(2 - hydroxyethyl) - p - phenylenediamine hydrochloride.

11. A method for dyeing human hair which comprises mixing the oxidation dye composition of Claim 1 with an oxidizing agent, applying an effective dyeing amount of the resulting mixture to human hair, and allowing said mixture to remain in contact with said hair for a period of time to effectively dye said hair.

12. A method for dyeing human hair which comprises mixing the oxidation dye composition of any one of Claims 2 to 10 with an oxidizing agent, applying an effective dyeing amount of the resulting mixture to human hair, and allowing said mixture to remain in contact with said hair for a period of time to effectively dye said hair.

13. An oxidation dye composition substantially as hereinbefore described.

14. An oxidation dye composition substantially as hereinbefore described in any one of the Examples.

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